

THE ASSESSMENT OF THE IMPACT OF THE APPLICATION OF BOTTOM SEDIMENTS AND THE BURDEN OF CADMIUM ON THE CONTENT OF THE RISK ELEMENTS IN THE SIMULATED BIOMASS OF FIELD PEA (*PISUM SATIVUM*, L.)

**TOTH T.¹, TOTH J.¹, KOPERNICKÁ M.¹, BYSTRICKA J.¹, STANOVIC R.¹, SLAVIK M.¹,
MUSILOVA J.¹, TREBICHALSKY P.¹, URMINSKA D.², HEGEDUSOVA A.³
and KAVALCOVA P.¹**

¹ Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences,
Department of Chemistry, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia

² Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences,
Department of Biochemistry and Biotechnology, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia

³ Slovak University of Agriculture in Nitra, Faculty of Horticulture and Landscape Engineering,
Department of Vegetable Production, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia
E-mail: tomas.toth@uniag.sk

ABSTRACT

Application of the decayed waste and bottom sediments has a positive effect on the state of soil hygiene, as a "blocker" intake of heavy metals. The aim of the study was to assess the level of cadmium of the transition observed in soil - plant system after bottom sediments application from water reservoirs Kolíňany in simulated conditions realized by bioassay, biological experiment. Plants of field pea were grown under simulated conditions in containers with the substrate (silica sand). It was added bottom sediment (BS) to silica sand (SS), which was taken from a water dam Kolíňany. Variants of the experiment: A: SS 1000 g + BS 0 g; B: SS 900 g + BS 100 g; C: SS 800 g + BS 200 g; D: SS 700 g + BS 300 g; E: 500 g SS + BS of 500 g. After six days from planting to all the variants we added 1,000 mg/kg Cd as Cd(NO₃)₂. The length of a biological experiment: 35 days. The endgame for the determination of risk analysis elements (Cd, Pb, Zn, Cu, Ni, Co) in the above ground and underground biomass of field pea was carried out using the method of the AAS (Varian 240 FS). In the above ground biomass of field pea after application 1000 mg/kg Cd into the substrate of all variants was the highest cadmium content in variant A (8,937.01 mg/kg). The lowest content of cadmium was in variant E (17.82 mg/kg), where 50% of the substrate formed the bottom sediment. The contents of zinc and copper were in the variants B - E 50 % lower those in the control variant A (without added BS). Correlation analysis of variant A after the addition of cadmium statistically significant ($P < 0.05$) confirmed the antagonistic relationship ($R = -0.99$) the ratio of the content of Zn : Ni in above ground biomass of field pea without application of sediment. In variant D was confirmed synergistic relationship ($R = 0.96$) the ratio of the content of Cd : Pb. In variant E was confirmed the antagonistic relationship ($R = -0.97$) the ratio of the content of Pb : Co. The contents of Zn and Cu in each of the variants have also been rising, the zinc content after application of Cd in variant B to E was the lower compared with the control. Correlation analysis in variant A was ($P < 0.05$) confirmed the synergistic relationship ($R = 0.99$) the ratio of the content of Cd : Zn and Cu : Ni. In variant D was statistically significant ($P < 0.05$) confirmed the synergistic relationship ($R = 0.97$) the ratio of the contents of the Cd : Cu and in variant E was statistically significant confirmed a synergistic relationship ($R = 0.99$) the ratio of the content of Cu : Co. In biological experiment after application of cadmium in dose 1000 mg/kg accumulation of cadmium was decreased in above ground biomass in the roots of pea varieties follows A>B>C>D>E.

Keywords: heavy metals, cadmium, field pea, contamination

1. Introduction

Bottom sediments contain nutritional pedomeliorating and agrochemical substances, which are suitable for the application to agricultural land. The sediments come in reservoir may contain toxic substances, especially heavy metals, which reduce possibility of their application not only to land but also on a wider scale. The use of bottom sediments for soil application can complicate the situation if they are contaminated with inorganic substances, whether natural or

anthropogenic origin and organic pollutants. Such contamination of bottom sediments has a significant impact not only on the quality of water, but also how to use them. It is one of the problems often presented in the form of an ecological time bomb. The content of contaminants in bottom sediment is the risk of the release and mobilization in the environment. Distributed biomass (biosludge, liquid, or solid fertilizer) contains many valuable mineral nutrients and can easily be used as a fertilizer in traditional agriculture (Urminská, 2013).

Degassed manure has several advantages in addition to traditional fertilizer. The anaerobic decomposition leads to lower loss of nutrients, as it is the case with traditional processing manure. Therefore, to achieve the same result should be less fertilizer. The biosludge significantly reduces the requirements for pesticides, improving the hydrophysical properties of the soil, which has a positive effect on hydrological regime of soil (Igaz, 2001).

Water reservoirs have an important role in the landscape and environment and they are an important element of water systems. The process of clogging reservoirs affects not only the capacity and lifetime of water facilities, but also the way they use and brings a number of problems, for example deterioration of stored water and the oxygen balance due to the decay of the organic fraction of sediments, which has a number of negative consequences (Fulajtár and Jánsky, 2001).

The bottom sediment is raw material of the bottom of dams, reservoirs or ponds. It is a raw material of natural processes and actually the washes of agricultural and forest soils, water flow and inflow powering water work or a series of dams. It has the essential characteristics of the surface layers of eroded soils (Holobradý and Il'ka, 1997; Torma *et al.*, 2008).

According to speed of flow and sedimentation and depth of water is the composition of bottom sediments identified as sandy gravels and sands or clay loam and clay material in most of the cases with a high content of organic matter. According to the grain composition is mainly used in construction to various building modifications or for the fertilization of agricultural soils (Gergeľová, 2008).

The sediment quality affects the water in the reservoir, but also the possibility of its further use. The sediments contain nutritional pedomeliorating and agrochemical substances which are suitable for the application to agricultural land, but they also come in reservoir may contain toxic substances, like heavy metals, which in turn decreases the possibility of application to the soil (Torma *et al.*, 2008).

One of the problems arising from the presence of contaminants in bottom sediments is the risk of the release and mobilization in the environment. The potentially toxic elements may be significantly toxic at low concentrations. Their presence in sediments may be a risk of negative changes in the quality of the soil after application (Gemici and Oyman, 2003; Šutriepka, 2007).

The toxicity of heavy metals in bottom sediments depends on factors, such as method of application to the soil, physical and chemical properties of the soil, climatic factors, and so on. The physicochemical property of soil that most significantly affects the toxicity of heavy metals is soil reaction (pH). The heavy metals are extremely mobile by the application to strongly acid soils, which facilitates their intake by plants. The effect of pH on biosorption of cationic dyes is similar as inorganic cations, since the mechanism is similar – organic cations are also bound to negatively charged functional groups exposed by cellular surfaces (Chojnacka, 2010). The application of the bottom sediments is recommended to the soil with a pH between 6.5 and 7.0 depending on the content of heavy metals in bottom sediments. The negative effect of heavy metals is more indicative of the granular slightly- crusted soil and soils with low organic matter content (Holobradý and Il'ka, 1997).

The concentration of certain trace elements, particularly their mobile forms, increase and can cause serious environmental threat, related to contamination and accumulation in soil, vegetation, animals, and in surface and ground waters (Alloway, 2005). By Petruzzelli *et al.* (1994) the impact of any metal in biosludge depends on its initial chemical state in the sludge, adsorption, precipitation mechanisms and humification processes that take place in the sludge. Zorpas *et al.* (2003) suggests that the application of large amounts of organic matter leads to

the growth of microbial population, which causes changes in the physicochemical properties within the mixture. By processes such as digestion, decrease of pH, creation of organic colloids or formation of humic complexes may be affected the distribution of heavy metals. The organic materials such as manure, biowaste or compost contain higher concentrations of trace elements than most of agricultural soils. The use of these organic materials cause the increasing of the total amounts of Cu, Zn, Pb, Cd, Fe and Mn in the soil (Reeves and Baker, 2000; McBride, 2004).

The intake of cadmium by plants, as other elements, depends on the quantity of soil properties which is confirmed by the authors Hanc *et al* (2009) and Bolan *et al* (2014) in their results, who pursued the effect of soil type to cadmium content in oat.

As well as the other heavy metals, the cadmium is taken by plants from the soil and accumulated mainly in roots. Even with a low level of soil contamination with cadmium is most contaminated leafy vegetables (lettuce, spinach), root vegetables (carrot, parsley, celery, beetroot) and brassica (kale, cabbage, radish) (Petříková, 1995; Feszterová and Jomová, 2012; Akinyele and Shokunbi, 2015).

An increased mobility of metals caused by anthropogenic pollution of soils may to increased their concentration in plants as a stress factor that causes physiological changes and growth inhibition even to the extinction of plants (Hegedüsová *et al.*, 2006; Rajkumar *et al*, 2009).

The population is exposed with different doses of cadmium depending on the way of entry, dose and time of exposure. The cadmium gets into the body by respiratory tract (15 to 30%), digestive system (4 to 7% in adults, absorption in children is higher) (Wexler, 1998).

The ions of Cd are incorporated into the body and have a destructive effect on the kidney and liver function. The highest concentrations of cadmium were in cereals, but also in molluscs and renal cortex (Raskin *et al*, 1994; Gamma *et al.*, 2006).

2. Material and methods

The experiment was realized by the form of a biological experiment under controlled conditions in Laboratory of Environmental Analyses and Foodstuffs in Dept. of Chemistry, SUA in Nitra. As plant material for pot experiment we chose field pea, variety Avola. Field pea (*Pisum sativum* L.) is a legume of the family Legumes (Fabaceae) with high level of protein, amino-acid composition and polysaccharides, that are usable source of energy and fiber.

Plants of field pea were grown under simulated conditions in containers with the substrate (silica sand). It was added bottom sediment (BS) to silica sand (SS), which was taken from water dam Koliňany. Chemical characterization of applied bottom sediment is: pH (KCl): 7.75; Cox: 2.07%; humus content: 3.4%; Ntotal: 1,925.0 mg/kg; Ca: 11,322.4 mg/kg; Mg: 712.04 mg/kg; K: 184.06 mg/kg; 19.96 mg/kg; Cd: 2.73 mg/kg; Pb: 18.9 mg/kg; Zn: 2.9 mg/kg; Cu: 18.88 mg/kg; Ni: 21,44 mg/kg and Co: 11,32 mg/kg.

Variants of the experiment: **A:** SS 1000 g + BS 0 g; **B:** SS 900 g + BS 100 g; **C:** SS 800 g + BS 200 g; **D:** SS 700 g + BS 300 g; **E:** 500 g SS + BS of 500 g. After six days from planting to all the variants we added 1000 mg/kg Cd as Cd(NO₃)₂. The length of a biological experiment: 35 days. Number of repetitions was 4 times. The endgame for the determination of risk analysis elements (Cd, Pb, Zn, Cu, Ni, Co) in the above ground and underground biomass (roots) of field pea was carried out an analysis to determine the total concentration of monitored heavy metals (Cd, Pb, Cu, Ni, Co and Zn) in extract of aqua regia. Mineralization of soil samples was done by 10 cm³ of aqua regia (2.5 cm³ HNO₃ and 7.5 cm³ HCl, Merck, Germany) using microwave digestion unit Mars X-press 5 (CEM Corp., USA) in closed PTFE vessels. Metal determinations were performed in a Varian AA240Z (Varian, Australia) atomic absorption spectrometer with Zeeman background correction. The graphite furnace technique was used for the determination of Cd and Pb. The content of copper and zinc were determined by Flame Atomic Absorption Spectrometry AA240FS Varian (Varian, Australia). All statistical analyses were carried out using the statistical software Statistica 12.0 (Statsoft, USA). We used Pearson correlation coefficients at significance level of p<0.05 (weak statistical significance) and p<0.001 (very strong statistical significance) to compare the impact of monitored parameters between them.

3. Results

Although heavy metal hyperaccumulation in plants was first reported in 1865 for *Thlaspi calaminare* (now *Thlaspi caerulescens*), the study of plant heavy metal hyperaccumulation is relatively recent. Although Cd is not an essential or beneficial element for plants, they generally exhibit measurable Cd concentrations, particularly in roots, but also in leaves, most probably as a result of inadvertent uptake and translocation (Assunção *et al.*, 2003). A foliar concentration above 100 µg.g⁻¹ DW (0.01 %) is considered exceptional and is used as a threshold value for Cd hyperaccumulation (Baker *et al.*, 2000; Pascaud *et al.*, 2015). The metal hyperaccumulation characteristic is not common in terrestrial higher plants and less than 0.2 % of all angiosperms have been identified as metal hyperaccumulators (Baker *et al.*, 2000). Hyperaccumulators of Ni, Zn, Cd, Pb, Cu, As, Co and Mn have been reported (Baker *et al.*, 2000; Ma *et al.*, 2001; Zhi *et al.*, 2015).

The cadmium content in biomass of field pea after application 1000 mg/kg of Cd into the substrate of all variants was the highest in the variant A (8937.01 mg/kg), where the substrate was silica sand and the lowest content was in the variant E (17.82 mg/kg), where 50% of the substrate was formed by bottom sediment. The accumulation of cadmium has been decreased by 500 times.

The addition of Cd to the substrate of all variants was reflected in various contents of risk elements in plant biomass. Risk elements at the different variants increasing and decreasing. The contents of the monitored risk elements (Zn, Cu, Ni and Co) were increased and decreased by the addition of bottom sediments into the substrate. The content of zinc and copper were in the variant B to E lower by half than in the control variant A without the addition of sediment after the application of Cd. The nickel content in variant B to E was lower by half compared to the control after application Cd. The cobalt contents after application of Cd into all variants were higher in the variant B, C, D compared to the control.

Correlation analysis of the variant A after application of cadmium was statistically significant ($P < 0.05$) confirmed an antagonistic relationship ($R = -0.99$) the ratio of the content of Zn : Ni in the biomass of field pea without the application of the sediment. In the variant D was confirmed the synergistic relationship ($R = 0.96$) the ratio of the content of Cd : Pb after 30% application of the sediment.

Table 1: The content of risk elements in the biomass and the roots of field pea after application 1000 mg/kg of cadmium (mg/kg)

prídavok	variant	plodina	Cd	Pb	Zn	Cu	Ni	Co
Cd	A		8937.01	8.95	86.26	57.56	5.73	0.72
	B		669.53	3.33	44.64	11.37	3.60	0.83
	C	above ground	204.49	6.70	46.09	13.24	3.86	1.01
	D	biomass	41.01	22.07	41.01	12.06	3.74	0.84
	E		17.82	6.71	48.73	12.58	3.46	0.63
Cd	A		18778.96	221.64	56.32	10.68	1.51	0.00
	B		10391.74	185.28	36.53	18.26	7.15	0.53
	C	roots	4583.17	829.71	38.32	17.38	9.88	1.19
	D		739.71	83.43	32.54	13.90	8.62	2.22
	E		70.52	240.42	40.55	17.75	7.85	1.92

In the variant E was confirmed the antagonistic relationship ($R = -0.97$) the ratio of the content of Pb : Co and Zn : Cu after 50% application of the sediment. In the variant D was confirmed the synergistic relationship ($R = 0.99$) the ratio of the content of Pb : Cu and antagonistic relationship ($R = -0.96$) the ratio of the content of Cu : Co after 30% application of the sediment, and in the variant V. was confirmed the synergistic relationship ($R = 0.95$) the ratio of the content of Zn : Cu in biomass of field pea after 50% application of the sediment. The cadmium content in roots of field pea, after application 1000 mg/kg of Cd to a substrate of all variants,

was the highest in the variant A (18,778.96 mg/kg), and the lowest content was in the variant E (70.52 mg/kg). The accumulation in pea roots has been decreased by 250 times.

The copper content was in the variants B, C, D and E was higher compared to the control after application of cadmium. Correlation analysis of the variant A after application of cadmium was statistically significant ($P < 0.05$) confirmed the synergistic relationship ($R = 0.99$) the ratio of the content of Cd : Zn and Cu : Ni in the root of field pea without the application of sediment, the synergistic relationship ($R = 0.97$) the ratio of the content of Cd : Cu in the variant D after 30% application of the sediment, and the synergistic relationship ($R = 0.99$) the ratio of the content of Cu : Co in the variant E after 50% application of the sediment.

The dynamics of monitored risk elements (Cd, Pb, Zn, Cu, Ni and Co) in the biomass and the roots of field pea according to the application of Cd and amounts of added sediment in the variants are confirmed by the findings of Baker *et al.* (2000), Hanc *et al.* (2009); Bolan *et al.* (2014),. It also confirmed by the findings of Raskin *et al.* (1994), Gergelova (2008), Bolan *et al.* (2014) that cadmium is taken from the substrate through the root system and accumulated in the roots, which in the case of biological experiment represent the ratio of accumulation 4-22:1, depending on the variant of the experiment.

4. Conclusions

The aim of our work was the assessment of the impact of bottom sediments to bioaccumulation ability of field pea after application 1000 mg/kg of cadmium by biological experiment of five different variants. In biological experiment after application of cadmium in dose 1000 mg/kg the accumulation of cadmium was decreased in above ground biomass and in the roots of pea depending on the variant follows $A > B > C > D > E$.

It was confirmed the fact that the accumulation of cadmium by plants is characterized by the root system and not in above ground biomass. The fertilization of agricultural crops by bottom sediments is the most common method of their use.

The application of organic sludge and bottom sediments has a positive effect on the state of soil hygiene, improves its structure and has an effect as a "blocker" of heavy metals intake because they bind to organic matter and thus become less available to plants.

ACKNOWLEDGEMENTS

This work was supported by the scientific project VEGA 1/0724/12, VEGA 1/0630/13 and KEGA 014SPU-4/201.

REFERENCES

1. Ma, L.Q. *et al.* (2001), A fern that hyperaccumulates arsenic. *Nature* 409: 579.
2. Assunção, A.G.L., *et al.* (2003), *Thlaspi caerulescens*, an attractive model species to study heavy metal hyperaccumulation in plants. *New Phytol.* 159:351-360
3. Akinyele I.O. and Shokunbi O.S. (2015), Concentrations of Mn, Fe, Cu, Zn, Cr, Cd, Pb, Ni in selected Nigerian tubers, legumes and cereals and estimates of the adult daily intakes, *Food Chemistry*, 173, 702–708.
4. Alloway, B. J. (2005), Bioavailability of elements in soils. In *Essential of medical geology*, (2005), Amsterdam. pp. 347-372.
5. Baker A. J. M. *et al.* (2000), Metal hyperaccumulator plants: a review of the ecology and physiology of a biological resource for phytoremediation of metal polluted soils. In: Terry N, Banuelos G (eds) *Phytoremediation of contaminated soil and water*. Lewis Publishers, Boca Raton, pp 85–108.
6. Bolan N. *et al.* (2014), Remediation of heavy metal(loid)s contaminated soils – To mobilize or to immobilize? *Journal of Hazardous Materials*, 2014, 266, 141– 166.
7. Chojnacka K. (2010), Biosorption and bioaccumulation – the prospects for practical applications. *Environment International*, 2010, 36, 299–307.
8. Feszterová M. and Jomová, K. (2012), Air as a factor affecting food hygiene, *Journal of Microbiology, Biotechnology and Food Sciences*, 2012, 1(4), 1109-1119.

9. Fulajtár, E. and Janský, L. (2001), Water erosion and erosion protection. Bratislava : VÚPOP, 2001 p. 310, ISBN 80-85361-85-X (in Slovak)
10. Gama, E. M. *et al* (2006), Preconcentration system for cadmium and lead determination in environmental samples using polyurethane foam (Me-BTANC. In Journal of Hazardous Material, vol.136, pp. 757-762.
11. Gemici, U. and Oyman, T. (2003), The influence of the abandoned Kalecik Hg mine on water and stream sediments (Karaburun, Izmir, Turkey). In The Science of The Total Environment, vol. 312, no 1, pp. 155-166.
12. Gergeľová, Z. (2008), Use of sewage sludge and bottom sediments in agriculture. Nitra: Agroinštitút, p. 28 s., ISBN 978-80-7139-126-5. (in Slovak)
13. Gill M. (2013) Heavy metal stress in plants: a review, International Journal of Advanced Research, 2013, 2(6), 1043-1055.
14. Hanc A. *et al* (2009), Changes in cadmium mobility during composting and after soil application. In Waste Management, doi: 10.1016/j.wasman.2009.03.027.
15. Hegedusová, A. *et al* (2006), Risks of soil contamination with cadmium. Scientific monograph, Edition: Prírodovedec N. 222., 89 p., ISBN: 80-8094-047-9. (in Slovak)
16. Holobradý, K. and Ilka, P. (1997) Methodology direct application of stabilized sewage sludge and bottom sediments on land. Bratislava: VÚPÚ (1997), p. 50. (in Slovak)
17. Igaz, D. (2001), Treatment of liquid organic waste and their use in the agricultural landscape of the fortress protecting the environment, SAU Nitra, pp. 25 (in Slovak)
18. McBride, M. B. (2003), Molybdenum, sulfur, and other trace elements in farm soils and forages after sewage sludge application. In Commun Soil Science Plant Anal, 35, pp. 517-535
19. Pascaud G. *et al* (2015), Particulate transport and risk assessment of Cd, Pb and Zn in a Wadi contaminated by runoff from mining wastes in a carbonated semi-arid context, Journal of Geochemical Exploration, 152, 27–36.
20. Petříková, V. (1995), Heavy metals in soils and crops in different localities exposed to air pollution. In Plant, Soil and Environment, 41 (1) pp. 17-23. (in Czech)
21. Petruzzelli, G. *et al* (1994), Characterization of heavy metal mobile species in sewage sludge for agricultural utilization. In Agrochimica (1994), 38, pp. 277-284
22. Rajkumar K.*et al* (2009), Effects of selected heavy metals (Pb, Cu, Ni, and Cd) in the aquatic medium on the restoration potential and accumulation in the stem cuttings of the terrestrial plant, *Talinum triangulare* Linn, Ecotoxicology, 2009, 18, 952–960.
23. Raskin I. *et al* (1994), E.Bioconcentration of heavy metals by plants, Current Opinion in Biotechnology, 1994, 5, 285–290.
24. Reeves R. D. and Baker A. J. M. (2000), Metal accumulating plants. In: Raskin I, Ensley BD (eds) Phytoremediation of toxic metals: using plants to clean up the environment. Wiley, New York, pp 193–230.
25. Šutriepka, M. (2007), Rating contaminated bottom sediments and water projects Ružín large Kozmálovce potentially toxic elements in accordance with the standards In Acta Environmentalica Universitatis Comenianae, 15 (1) pp. 58-65, ISSN 1335-0285. (in Slovak)
26. Torma, S., *et al* (2008), Possibility of using cleaned water from sewage for irrigation of agricultural land. Bratislava: VÚPOP, p. 301-308. ISBN 978-80-89128-49-5. (in Slovak)
27. Urminská, J. (2013), The risk of influence of copper to the environment in burdened territory by anthropogenic activities from contaminated sediments. Acta Facultatis Ecologiae, 28: 79-88
28. Wexler, P. (1998), Encyclopedia of Toxicology. Inc.,U.S.: Academic Press 1705, ISBN-10 012227220X.
29. Zhi Y. *et al* (2015), Influence of Heavy Metals on Seed Germination and Early Seedling Growth in *Eruca sativa* Mill, American Journal of Plant Sciences, 2015, 6, 582-590.
30. Zorpas, A. A. (2003), Waste paper and clinoptilolite as a bulking material with dewatered anaerobically stabilized primary sewage sludge (DASPSS) for compost production. In Waste Manage, 23, pp. 27-35.